Kinetic studies and optimization of abies wood fractionation by hydrogen peroxide at mild conditions with TiO_2 catalyst

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Abstract

The kinetic study of abies wood delignification by H_2O_2 in the medium acetic acid – water was firstly studied in the presence of TiO_2 catalyst under mild conditions: temperatures 70 – 100 °C, atmospheric pressure. The oxidative delignification process is described satisfactory by the first order equation in all temperature range. The rate constants are varied between 0.12 – 1.72 $\cdot 10^{-4}$ s^{-1} and the activation energy is near 81 $KJ \cdot mol^{-1}$.

By experimental and numerical optimization the parameters of delignification process providing the effective fractionation of abies wood on microcrystalline cellulose and soluble lignin were established.

Key words: abies wood, oxidative fractionation, hydrogen peroxide, TiO_2 catalyst, kinetics, optimization.

Introduction

Manufacture of cellulose by sulfate and sulfide pulping is the mist developed direction of the chemical processing of wood [1, 2]. These industrial pulping processes are based on the application of harmful and corrosive sulfur and chlorine-containing delignification reagents. Advanced processes of organosolv delignification, which use the organic and water-organic solvents, can become an alternative to traditional pulping [3-5]. The most promising solvents free from sulfur and chlorine are the organic acids (acetic and formic acids), alcohols (methanol, ethanol, butanol), acetone and other non-toxic organic compounds [6-9]. Organosolv methods of delignification cause the less environmental damage and they are less energy-intensive as compared to existing technologies.

In recent years the much attention is paid to the processes of organosolv delignification in the presence of environmentally safe oxidants, like oxygen and hydrogen peroxide [10-12]. The new organosolv processes do not always allow obtaining the required quality cellulose for further chemical processing. But they can be successfully used for wood fractionation on cellulose and lignin for subsequent processing of cellulose to chemicals and biofuels. It has been shown that some catalysts are able to speed up the processes of organosolv delignification [13-14].

Some complexes of the transition metals for example so-called polyoxometalates, can promote the processes of pulp and wood delignification by oxygen [15, 16]. However the practical use of these catalysts is complicated by their high cost and complexity of regeneration for the reuse.

Sulfuric acid can act as a catalyst of wood [17] oxidative delignification by H_2O_2 in acetic acid–water solvent. But, at the same time, H_2SO_4 promotes the hydrolysis of polysaccharides decreasing of the yield of cellulosic product. Besides, H_2SO_4 catalyst has such technological disadvantages as high toxicity and corrosion activity.

The more technologically convenient solid TiO_2 can catalyze an oxidative delignification of wood by H_2O_2 at 120–130 °C and elevated pressure [18, 19]. Advantages of TiO_2 application as delignification catalyst are stipulated by the absence of corrosion activity and toxicity, by its availability, low cost and lack of need for its

regeneration. It worth to note, that catalytic properties of TiO_2-based materials are sensitive to the method of its producing [20].

The different side reactions of low molecular mass products condensation with the formation of so-called "pseudo-lignin" [21] take place in wood delignification processes at elevated temperatures. The contribution of condensation reactions can be reduced by the acceleration of a diffusion of lignin depolymerization products from wood particles into solution.

In previous papers [22] the authors have shown that the use of small particles of wood (sawdust), the high liquid to wood ratio (LWR) and the intensive mixing of the reaction solution allows to eliminate the externally diffusion limitations and to provide a high rate of aspen wood delignification by H_2O_2 under mild conditions (70–100 °C, atmospheric pressure) in the presence of 2 % H_2SO_4 catalyst.

The present work demonstrate the possibility of successful replacement under mild conditions the H_2SO_4 catalyst on non-toxic and non-corrosive solid TiO_2 catalyst in the oxidative fractionation of abies wood on cellulose and soluble lignin. The kinetic study of abies wood sawdust delignification in the medium "H_2O_2–CH_3COOH–H_2O–TiO_2 catalyst" at temperatures 70–100 °C, atmospheric pressure and under vigorous agitation (700 rpm) was accomplished. By experimental and computation methods the optimal process conditions providing a high yield of quality cellulosic product were determined.

Experimental

Air dry sawdust (fraction 2-5 mm) of abies (*Abies sibirica L.*) wood harvested in the forest area near Krasnoyarsk city has been used as initial raw material. The chemical composition of abies wood (% wt. on abs. dry wood): cellulose – 45.7, lignin – 25.3, hemicelluloses – 17.7, extractive substances – 6.2, ash – 0.5.

The delignification solution was composed of the "chemically pure" acetic acid (GOST 61-75), "medical grade" hydrogen peroxide (GOST 177-88) and distilled water (GOST 6709-72). All chemical reagents were purchased in CJSC "Khimreactivsnab" (Russia).

Commercial TiO_2 (GOST 9808-84) with an average particle size of about 10 microns and BET surface area 3 m^2 /g was used as the catalyst.

Delignification of wood sawdust was carried out using 250 cm^3 glass reactor equipped with mechanical stirrer, reflux condenser and thermometer. Abies wood sawdust (10 g) was placed to glass reactor. Then, a mixture of glacial acetic acid (98 % wt.), hydrogen peroxide (32 % wt.), distilled water and TiO_2 was added. The reaction mixture was vigorously stirred (700 rpm) at selected temperature (70–100 °C) during 1–4 h. Composition of the reaction mixture was varied in the following range: hydrogen peroxide 3–7 % wt., acetic acid 15–40 % wt., liquid/wood ratio (LWR) –10–15. Concentration of TiO_2 catalyst was at 1 % wt. in all experiments. The reaction temperature was kept by thermostat "Termex". When the reaction was completed, the solid product was separated under vacuum using Buchner funnel, following by washing distilled water and drying at 105 °C until constant weight.

Such parameters as the residual lignin and hemicelluloses content in cellulosic product were used to evaluate the delignification activity of TiO_2 catalyst.

The cellulosic product yield was estimated by weight method and calculated as follows:

$Y = (m/m_o) \times 100$, where Y – yield of cellulosic product, % wt.; m – mass of abs. dry cellulosic product, g; m_o – mass of abs. dry wood, g.

The content of cellulose, lignin and hemicelluloses was defined by generally accepted chemical methods in wood chemistry [23].

X-ray diffraction analysis was carried out on PANalytical X'Pert Pro diffractometer using Cu-Ka source (A = 0,154 nm) in the 2θ range 5–70 ° and scanning step width of 0,01 °/scan. The cellulose samples were analyzed by the powder method in cuvette with 2,5 cm diameter. Crystallinity index (CI) was calculated from the ratio of the height between the intensity of the crystalline peak ($I_{002} - I_{AM}$) and total intensity (I_{002}) after subtraction of the background signal [25]: $CI = (I_{002} - I_{AM}) / (I_{002})$, where I_{002} – is the height of the 002 peak (I_{002}); I_{AM} – is the height of the minimum between the 002 and the 101 peaks.

Infrared spectroscopy analysis (FTIR) was carried out in transmission mode. Samples of cellulose (4 mg for each) were prepared in tablet with matrix KBr. The spectra were recorded with Bruker Tensor – 27 wavelength in the range 4000–400 cm^{-1}. Spectral data were processed by the program OPUS/YR (version 2.2).

Result and discussion

To optimize the process of abies wood delignification the influence of reaction conditions (temperature, concentrations of acetic acid and hydrogen peroxide, liquid/wood ratio, time) on the yield and composition of cellulosic product was studied.

The influence of H_2O_2 and CH_3COOH concentration on the yield and composition of cellulosic products obtained by abies wood delignification with 1 % TiO_2 catalyst was studied at the fixed temperature, LWR and time.

The increase of H_2O_2 concentration in the reaction mixture from 3 to 5 % mas. significantly reduces the content of residual lignin and of hemicelluloses in the cellulosic product (Table 1). But at the same time the yield of cellulosic products is decreased from 69.7 % mas. to 52.6 % mas. The same regularities were observed with the increase of acetic acid concentration (Table 2).

Table1 Impact of H_2O_2 concentration on the yield and composition of cellulosic products obtained by abies wood delignification at 100 °C, CH_3COOH – 30 % mas., LWR – 15, time – 4 h

Concentration of H_2O_2, % mas.	Yield of cellulosic product*, % mas	Composition of cellulosic product**, % mas.		
		Cellulose	Lignin	Hemicelluloses
3	69.7	73.0	15.4	11.1
4	56.5	88.7	3.9	7.9
5	55.0	93.2	2.1	4.4
7	52.6	94.1	1.8	3.8

* – on abs. dry wood, ** – on abs. dry cellulosic product

Table 2 Impact of CH_3COOH concentration on the yield and composition of cellulosic products obtained by abies wood delignification at 100 °C, H_2O_2 – 6 % mas., LWR – 15, time – 4 h

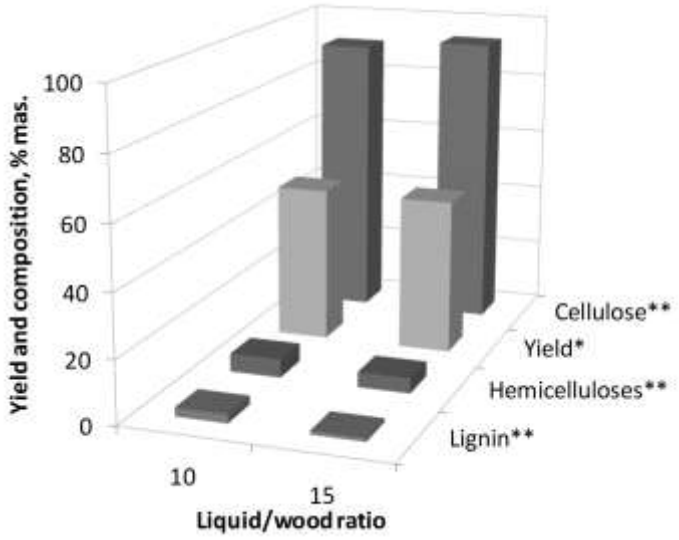
Concentration of CH_3COOH, % mas.	Yield of cellulosic product*, % mas	Composition of cellulosic product**, % mas.		
		Cellulose	Lignin	Hemicelluloses
20	58.9	83.2	9.5	6.9
25	55.2	90.2	3.2	6.2
30	52.6	91.6	2.3	5.7
35	52.0	93.7	2.2	3.7

* – on abs. dry wood, ** – on abs. dry cellulosic product

Acetic acid was used in the reaction mixture to facilitate the dissolution of the products of lignin oxidative depolymerization. When CH_3COOH concentration in reaction medium is less than 20 % mas. the obtained cellulosic product has a high content of residual lignin.

The rather high LWR (10–15) was used in the experiments in order to reduce the external diffusion limitations. The increase of LWR from 10 to 15 only slightly affects on the yield and composition of cellulosic

product (Fig. 1). In this case the content of residual lignin is decreased from 2.8 % mas. to 1.1 % mas. and that of hemicelluloses – from 5.9 % mas. to 4.8 % mas.



* on abs. dry wood, ** on abs. dry cellulose product

Fig. 1 Influence of liquid/wood ratio on the yield and composition of cellulosic product from abies wood: CH_3COOH – 30 % mas.; H_2O_2 – 6 % mas.; temperature – 100 °C; time – 4 h

The kinetic study of abies wood delignification by H_2O_2 in the temperature range 70–100 °C was accomplished. The variation of lignin concentration in the cellulosic product was used for calculating the rate constants of delignification process. It was found that the process of oxidative delignification of abies wood by H_2O_2 in the presence of TiO_2 catalyst is described satisfactory by the first order equations in the range 70–100 °C (Fig. 2).

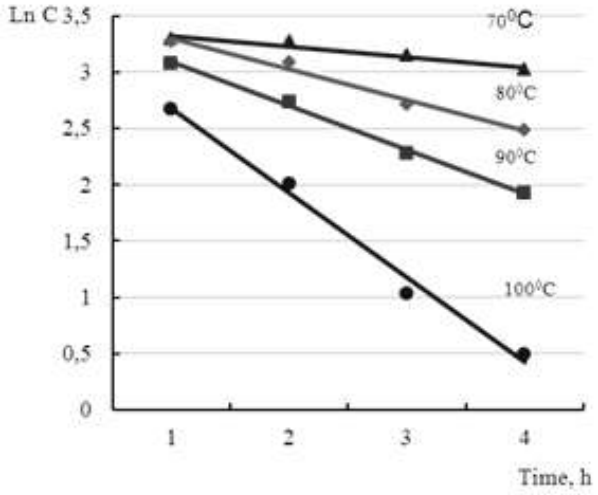


Fig. 2 Time dependence of the logarithm of lignin content in cellulosic products, obtained by abies wood oxidative delignification with TiO_2 catalyst, H_2O_2–6 % mas., CH_3COOH – 30 % mas., LWR – 15

The calculated rate constants of abies wood oxidative delignification with catalyst TiO_2 are presented in Table 3.

Table 3 Rate constants of abies wood delignification process (delignification conditions are the same as in Fig. 2)

Temperature, °C	$k \times 10^{-4}$, s^{-1}	R^2
70	0,12	0,93
80	0,43	0,98
90	0,79	0,99
100	1,72	0,98

The value of activation energy of abies wood oxidative delignification process was determined using temperature dependence of the rate constants in Arrhenius coordinates (Fig. 3). The rather high value of activation energy (81 kJ·mol^{-1}) points on the absence a noticeable effect of external diffusion limitations at the used conditions of abies wood oxidative delignification with TiO_2 catalyst.

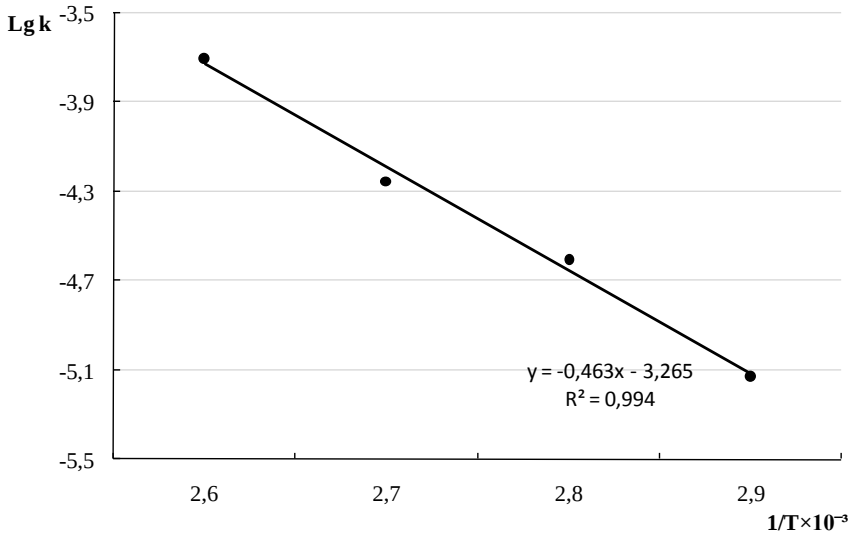


Fig. 3 Temperature dependence of rate constants of abies wood oxidative delignification process with TiO_2 catalyst (CH_3COOH – 30 % wt., H_2O_2 –6 % wt., LWR = 15, time – 4 h)

The similar kinetic parameters of oxidative delignification of aspen wood [22], birch wood [25] and abies wood in the presence of H_2SO_4 and TiO_2 catalysts (the first order equations, the comparable values of activation energies 82–91 kJ·mol-1) point on the identical mechanism of this delignification processes.

It is known that different homolytic and heterolytic reactions involved in the oxidative destruction of lignin can take place simultaneously [26]. The obtained results and the literature data suggest that the oxidative destruction of lignin in the acetic acid-hydrogen peroxide-water medium is accomplished via homolytic route in the presence both H_2SO_4 and TiO_2 catalysts. Above mentioned catalysts initiate hydrogen peroxide decomposition yielding hydroxyl and peroxyl radicals. These radicals are very active in oxidative degradation of organic substrates via the homolytic mechanism [29].

Probably the dissolved H_2SO_4 catalyst executes the catalytic action through its adsorption on functional groups of lignin. In the case of the solid catalyst TiO_2, an indirect catalytic route is possible. The hydroxyl and peroxyl radicals generated from H_2O_2 on the TiO_2 surface can diffuse through the liquid reaction medium to the wood particle surface and to execute the oxidative destruction of lignin.

The numerical optimization of the abies wood oxidative delignification process with TiO_2 catalyst was carried out with the application software Statgraphic according to earlier described procedure [28]. The main purpose of the analysis was to find conditions for the most complete removal of lignin from wood while maintaining a sufficiently high yield of cellulosic product.

As in dependent variables, the following factors have been selected: X_1 – the H_2O_2 concentration in reaction solution, % mas.; X_2 – liquid to wood ratio. The other process parameters were fixed: temperature 100 °C, concentration of acetic acid 30 % mas.; TiO_2 1 % mas., time 4 h.

The following output parameters for optimization were selected: Y_1 – the cellulosic product yield, % mas.; Y_2 – the cellulose content in the product, % mas.; Y_3 – lignin content in the product, % mas.

Optimization was performed with the use of generalized parameter of optimization (W_a) which was calculated using the following equation:

$$Wa = \frac{\sum_{j=1}^{p} \delta j dj}{\sum_{j=1}^{p} \delta j}$$

where δ – the weight of the output parameter $0 \le \delta_j \le 1$; d_j – private utility function which was calculated using the following equation:

$$dj = \frac{\phi_o(x) - y_j^{(-)}}{y_j^{(+)} - y_j^{(-)}}$$

where $\varphi_0(x)$ – the response of output parameter at the point X; ; $y_j^{(+)}$ и $y_j^{(-)}$ – the best and worst values of the output parameters within the studied region.

Table 4 presents the data on conditions and results of experiments for the calculation of generalized parameter of optimization. When choosing the weights δ assumes that the residual lignin content is the most important parameter for assessing the quality of cellulosic product. For this reason this parameter got the weight equal 1. The weights of such parameters as yield of cellulosic product and cellulose content in the product were choosing equal 0.5.

Table 4 Matrix for planning of the experiments of abies wood delignification, the results of dispersion analysis, the utility functions and the generalized parameter of optimization

Experimental number	X_1	X_2	Y_1	Y_2	Y_3	d_1	d_2	d_3	Wa
1	2	5	76.8	71.0	21.8	1	0	0	0.25
2	4	5	72.6	73.6	19.2	0.858	0.126	0.126	0.309
3	6	5	63.8	78.9	13.9	0.560	0.385	0.385	0.428
4	2	10	64.9	76.4	16.4	0.597	0.263	0.263	0.346
5	4	10	51.2	87.6	5.2	0.135	0.809	0.809	0.640
6	6	10	47.7	89.1	3.7	0.017	0.883	0.882	0.666
7	2	15	56.6	84.3	8.8	0.317	0.648	0.634	0.558
8	4	15	49.9	90.3	2.5	0.091	0.941	0.941	0.728
9	6	15	47.2	91.5	1.3	0	1	1	0.75
$Y^{(-)}$			47.2	71.0	21.8				
$Y^{(+)}$			76.8	91.5	1.3				
δ			0.5	0.5	1				

Table 5 shows the results of analysis of variances on the influence of the main factors on the generalized parameter of optimization W_a.

Table 5 Analysis of variances for W_a.

Dispersion source	Sum of squares	df	F-Ratio	P-Value
A:X1	0.07935	1	15.60	0.0289
B:X2	0.1834	1	36.07	0.0092
AA	0.00704	1	1.38	0.3242
AB	0.000049	1	0.01	0.9280
BB	0.004386	1	0.86	0.4215

F-ratio Variances (F-Ratio) and the level of significance (P-Value) characterize the contribution of each factor in the outcome of the process. Contribution of factor is more significant when the F-Ratio is greater and the significance level (P-Value) is smaller.

Analysis of variances showed that the effect of both factors X_1 and X_2 on the generalized parameter of optimization is statistically significant (P-Value less than 0.05, that is, the confidence level is above 95%, which is considered a good result in technological research).

As a result of mathematical processing the following regression equation was obtained:

$$W_a = 0.5990 + 0.115X_1 + 0.1748X_2 – 0.0593\ X_1^2 + 0.0035X_1X_2 - 0{,}0468X_2^2$$

Response surface of the generalized parameter of optimization is presented on Fig. 4.

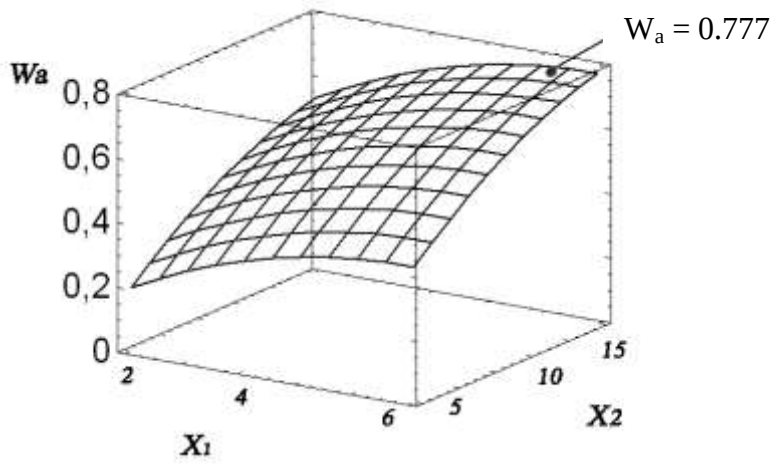


Fig. 4 Response surface of the generalized parameter (W_a) of the optimization of abies wood delignification with TiO_2 catalyst: X_1 – initial concentration of H_2O_2, X_2 – liquid to wood ratio

It was found that the generalized parameter of optimization abies wood oxidative delignification process is set to 0.777. This compiles with the following optimal parameters of delignification process at fixed temperature 100 °C: concentrations of H_2O_2 in reaction solution 5.9 % mas. and of CH_3COOH 30 % mas., LWR 15, duration 4 h.

Cellulosic product obtained by oxidative delignification of abies-wood sawdust at optimal parameters was studied by XRD and FTIR methods.

The FTIR spectra of cellulosic product from abies wood and the commercial sample of MCC Vivapur are very similar (Fig. 5).

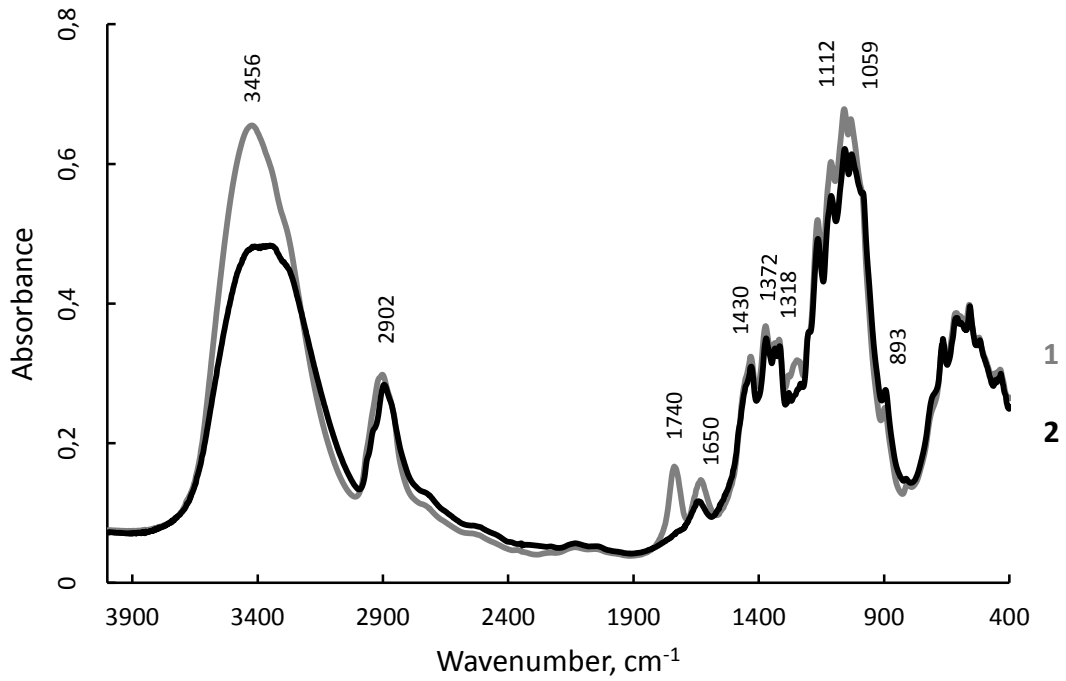


Fig. 5 FTIR spectra of cellulosic product from abies wood (1) and of commercial MCC Vivapur (2)

Both samples have an absorption bands attributed to microcrystalline cellulose [29, 30]. The absences in the spectrum of cellulosic product from abies wood the peaks in the range 1509–1609 cm^{-1}, which would correspond to C = C aromatic skeletal vibrations, indicate the complete removal of lignin from cellulosic product. The absorption band which corresponds to either the acetyl or uronic ester groups of hemicelluloses normally appears in the region 1700–1740 cm^{-1} [31]. The presence of this band in spectrum of cellulosic product from abies wood indicates that some part of hemicelluloses was not removed during abies wood delignification with H_2O_2 at 100°C.

The absorption peak at 1430 cm^{-1} corresponds to CH_2 bending vibration that attributed to the "crystallinity band" in the cellulose [32]. The band at 893 cm^{-1} was attributed to the C-O-C stretching vibration of β- (1→4) – glycosidic linkages of cellulose, which was considered as an "amorphous band" in the cellulose [32]. The ratio of peak areas A_{1430}/ A_{893} was proposed as sensible to cellulose type I crystallinity [33]. Practically the same values of this ratio for cellulose from abies wood (1.13) and for commercial MCC Vivapur (1.12) indicate the similar structures of the both samples.

According to X-ray diffraction data the cellulose from abies wood and the commercial MCC Vivapur have a crystal lattice typical for cellulose I [34] and the crystallinity indexes 0.70 – 0.75.

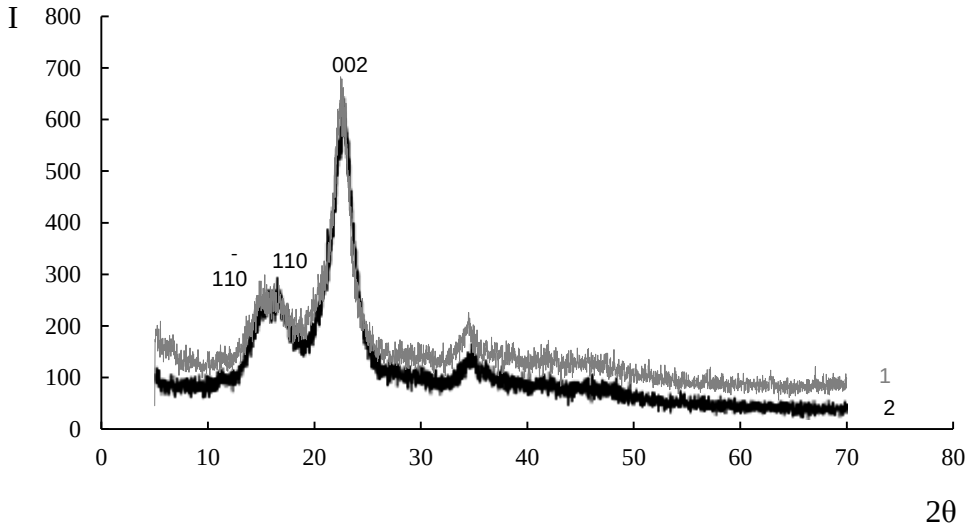


Fig. 6 X-ray diffraction patterns of cellulose from abies wood (1) and of the commercial MCC Vivapur (2)

Conclusion

The reduction of diffusion limitations by reducing the size of abies wood particles and by the use of intensive agitation of the reaction mixture allowed to decrease the temperature of wood delignification by H_2O_2 with TiO_2 catalyst and to provide its effective fractionation on microcrystalline cellulose and soluble lignin.

The kinetic study of abies wood delignification by H_2O_2 in the medium acetic acid – water was firstly studied in the presence of TiO_2 catalyst under mild conditions: temperatures 70 – 100 °C, atmospheric pressure. The oxidative delignification process is described satisfactory by the first order equation in all temperature range.

The rate constants are varied between 0.12 – 1.72 $\cdot 10^{-4}$ s^{-1} and the activation energy is near 81 KJ$\cdot$mol^{-1}.

By experimental and numerical optimization the parameters of delignification process providing a high yield (53.3 % mas.) of quality cellulosic product were established: temperature 100 °C, concentration of H_2O_2 5.9 % mas., of CH_3COOH 30 % mas., LWR 15, duration 4 h.

According to XRD and FTIR data the cellulose obtained by abies wood oxidative delignification with 1 % mas. TiO_2 catalyst has the structure of microcrystalline cellulose.

Acknowledgements

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